

REMARKS

In the Office Action dated 23 March 2004, claims 13-29, all claims pending in this application, had been rejected and the rejection had been made Final. Applicants have not amended the claims, but proffer the remarks to follow in traversal of the stated ground for rejection.

All claims had been rejected under 35 USC 112, second paragraph,. As explained, the rejection is based upon the theory that "one cannot unambiguously discern the precise manner in which the variously recited polyamides and copolyamides have been "modified" (emphasis added).

Firstly, the claims are directed to a wave guide including a protective sheath made from a modified PA. The modified PA has been characterized by the concentration of amino terminal groups and carboxyl terminal group. These concentrations and the ratios thereof uniquely characterize the PA's used to implement the invention and can be identified readily by analysis of the claimed wave guide and sheath. How or where they are obtained is not critical and neither the method of making nor the unique PA's are claimed. The surprising advantage when used in this way is the genesis of the invention.

Secondly, methods are available and the claims are enabled.

Enclosed with this response are pages 470-471 of Vo. 19 of the *Kirk-Othmer Encyclopedia of Chemical Technology*, Fourth ed. which describes methods of synthesis of polyamides. It is noted that the "normal" ratio of amino to carboxyl terminals would be approximately 1:1 in the absence of regulators (pg. 471, 1st paragraph).

The functioning of different regulators for the production of polyamide 6 from ϵ -caprolactam is described by Mizerovskii, L.N. and Paikachev, Yu. S. in *Polym. Sci. U.S.S.R.* 12 (1970), pp 858-869. On page 859 there is described that by using a monocarboxylic acid as the regulator, there will be formed three kinds of terminal groups: amino terminal groups, carboxylic terminal groups and amide terminal groups (RCONH-).

The amide terminal groups are formed by the classical reaction of the monocarboxylic acid (RCOOH) with an amino terminal group. Therefore, the addition of monocarboxylic acid reduces the number of amino terminal groups. If a dicarboxylic acid is used, not only the number of amino terminal

groups is reduced, but also the number of carboxyl terminal group is increased, since ultimately one amino terminal group is replaced by one carboxyl group.

If a monoamine (RNH_2) is used as a regulator, it reacts with a carboxyl terminal group forming an amide group (RNHOC-). Therefore, the addition of a monoamine reduces the number of carboxyl terminal groups. If a diamine is used, a carboxyl group is replaced by an amino group and therefore the number of amino terminal groups is increased.

In the case of the modified polyamides described in the present application, the modification is made by using a basic regulator (amine) instead of an acidic regulator (carboxylic acid) for producing the polyamides.

Therefore, a reversion of the terminal group ratio occurs, as shown in the Table below for two polyamide 12's. By using an amine regulator (hexamethylenediamine) the amino terminal group concentration is made to predominate, whereas by using a carboxylic acid as a regulator, the carboxyl terminal group concentration is made to predominant.

TABLE

	Unmodified Polyamide 12	Modified Polyamide 12
Commercial Name	Grilamid L16	Grilamid L16A
Regulator amount* [wt.-%]	0.63	0.61
Amino Terminal Group Concentration [meq/kg]	10	100
Carboxyl Terminal Group Concentration [meq/kg']	95	12
Rel. Viscosity 0,5% in M-cresol, 20°C	1.65	1.67

Also attached are product summaries for Grilamid L16 and L16M (not this invention) and L16A (this invention). Not that the Technical Data Sheet is not yet available. The products are different, have

different properties and produce surprisingly different results in the wave guide, as shown in the examples.

The claims (except 19) were rejected as obvious over Yamamoto et al., U.S. Patent No. 4,593,974 in view of Yang et al., U.S. Patent No. 6,064,790. The correctness of this rejection depends upon the proper interpretation of column 4, lines 12-32, of Yang et al. As explained supra, the examples in the reference have not the same composition or properties of the PA as modified to have the properties of the polyamides with the amino to carboxyl terminal ratios as claimed. There can be no expectation that such a change in ratios would result in the dramatically improved properties. Apparently, the European Examiner agreed as indicated by the International Search Report for the underlying priority application published as WO 00/60382.

In view of the arguments presented, the rejections are traversed and the matter is in condition for allowance. Passage to issue is respectfully solicited.

Enclosure: *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 19, pp 470-471
Polym Sci USSR (1970) , pp. 558 - 569
International Search Report, WO 00/60382
Product Sheets

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

KIRK-OTHMER

ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

FOURTH EDITION

VOLUME 19

PIGMENTS
TO
POWDERS, HANDLING



A Wiley-Interscience Publication

JOHN WILEY & SONS

New York • Chichester • Brisbane • Toronto • Singapore

470 POLYAMIDES (GENERAL)

Vol. 19

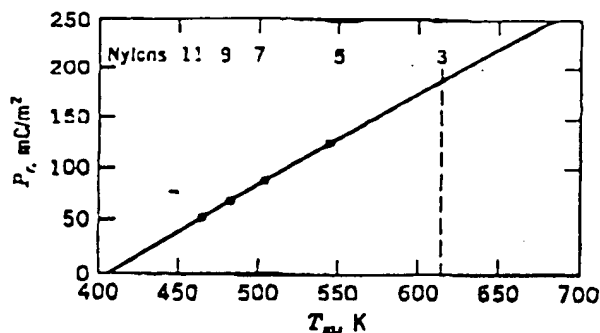
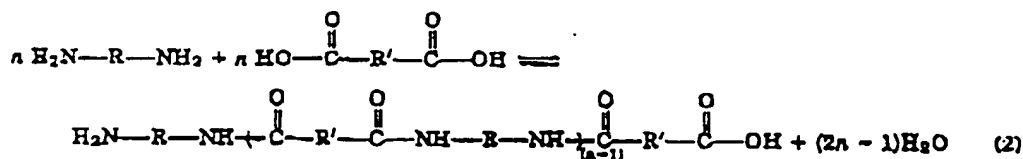
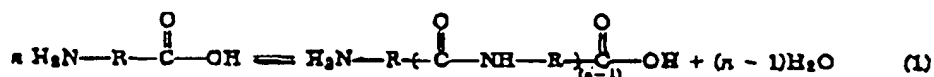


Fig. 5. The dependence of remanent polarization, P_r , on the melting point, T_m , in odd nylons (40).

Chemical Properties

PREPARATION

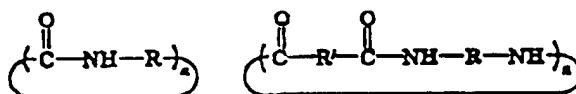
Direct Amidation. The direct reaction of amino acids to form Type AB polyamides (eq. 1) and diacids and diamines to form type AABB polyamides (eq. 2) are two of the most commonly used methods to produce polyamides. The



integer n is called the degree of polymerization (DP). The average DP is approximately 200 for a typical nylon-6, or about 100 for nylon-6,6; thus the number-average molecular weight is approximately equal for both, since the monomer, hexamethylenedipamide, for nylon-6,6 has twice the unit weight as the monomer, ϵ -aminocaproamide, has in nylon-6. Water is released as a by-product of the reaction and depending on the conditions of the reaction can be in equilibrium with the reactants. Ideally for the amino acids, only one homologous series of linear polymers is formed, each member of which possesses one amino and one carboxyl end group, as shown in equation 2. However, for the type ABB polymers, two additional homologous series of linear polymers are possibly one with two amino end groups and one with two carboxyl end groups:



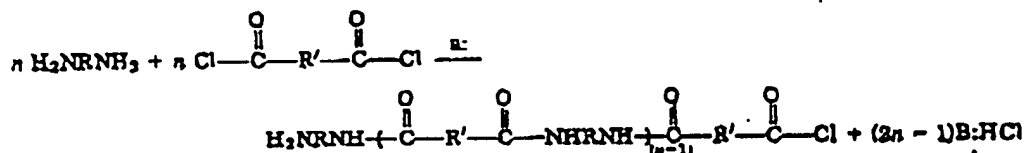
Polymers from either of these homologous series can be made to predominate by using a small excess of the diamine or diacid, respectively. In addition to these linear polymers, cyclic oligomers are also formed, though in this case n



is generally <10 for type AABB and <20 for type AB polymers. Thus, for the Type AB polyamides, direct polyamidation leads ideally to a mixture of two homologous series of polymers, one linear and one cyclic, and for the Type AABB a mixture of four is formed, three linear and one cyclic. Additional complications can arise as a result of side reactions and degradation, which can lead to different end groups, defects along the chain, or branching.

Direct amidation is generally carried out in the melt, although it can be done in an inert solvent starting from the dry salt (46). Because most aliphatic polyamides melt in the range of $200\text{--}300^\circ\text{C}$ and aromatic-containing polyamides at even higher temperatures, the reactants and products must be thermally stable to be polymerized via this method.

Acid Chloride Reaction. In situations where the reactants are sensitive to high temperature or the polymer degrades before the melt point is reached, the acid chloride route is often used to produce the polyamide (47). The basic reaction in the presence of a base, B:, is as follows:



Because almost any diacid can be readily converted to the acid chloride, this reaction is quite versatile and several variations have been developed. In the interfacial polymerization method the reaction occurs at the boundary of two phases: one contains a solution of the acid chloride in a water-immiscible solvent and the other is a solution of the diamine in water with an inorganic base and a surfactant (48). In the solution method, only one phase is present, which contains a solution of the diamine and diacid chloride. An organic base is added as an acceptor for the hydrogen chloride produced in the reaction (49). Following any of these methods of preparation, the polymer is exposed to water and the acid chloride end is converted to a carboxylic acid end. However, it is very difficult to remove all traces of chloride from the polymer, even with repeated washings with a strong base.

Ring-Opening Polymerization. Ring-opening polymerization is the method used to convert lactams to polyamides. There are several variations of the method, but the most commonly practiced method in industry is hydrolytic polymerization, in which lactams containing six or more carbons in the ring

REGULATION OF MOLECULAR WEIGHT OF POLYCAPROAMIDE*

L. N. MIKROVSKIY and YU. S. PAIKACHEV

Chemical Technology Institute, Ivanovsk

(Received 30 December 1968)

IN ORDER to obtain polycaprolactam (PCA) with a definite molecular weight, molecular-weight regulators are introduced into the monomer before polymerization: these are mono- and dicarboxylic acids, mono- and diamines, amine salts of carboxylic acids, strong acids and bases, and amine salts of strong acids.

By interacting with one or both end groups of PCA, these compounds terminate the propagating chain through the formation of end alkyl- or arylamide groups, or through salt formation.

In order to assess the degree of polymerization (\bar{P}) of PCA synthesized in the presence of regulators, the ratio

$$\bar{P} = 100/q, \quad (1)$$

is generally used [3, 4], where q is the quantity of regulator in mole % of the quantity of caprolactam. Agreement between theory and experiment is thus found only in the presence of at least 2 mole % of regulator [4, 5], and the discrepancy between the calculated and experimental values of \bar{P} with smaller quantities of regulator is usually explained by the uncontrolled termination of the chain through impurities in the caprolactam.

It should, however, be remembered that regulation of the molecular weight of PCA (and also of other polyamides) is also possible in the absence of special substances because of the reversibility of the polyamidation reaction



In this case, the degree of polymerization of PCA is determined by the equation [6-9]:

$$\bar{P} = \sqrt{\frac{K}{m}}, \quad (2)$$

where K is the constant for the amide equilibrium and m is the equilibrium concentration of water in moles per mole of the chemical unit of the macromolecule.

Since it is practically impossible to obtain an absolutely dry melt of PCA under laboratory conditions, and even more so under industrial conditions, the

* Vysokomol. soyed. A12: No. 4, 761-770, 1970.

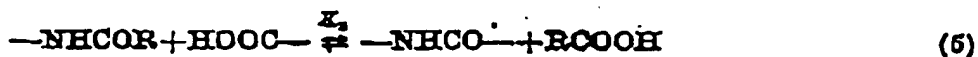
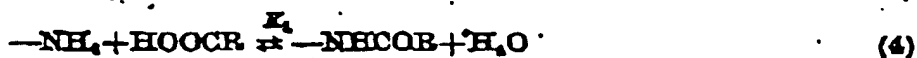
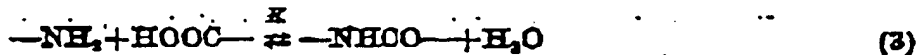
effect of the reversibility of polyamidation on the degree of polymerization of PCA synthesized in the presence of a regulator must clearly not be neglected. In fact, the regulator is usually introduced at the rate of 0.2-1 mole % [2, 8], and the water content in the PCA melt at the end of the reaction amounts to 1-2 mole % (0.15-0.26 wt. %) [10]. Under these conditions, \bar{P} for the polymer should depend both on the amount of water and also on the amount of regulator. It is therefore undoubtedly of interest to establish the quantitative connection between the average degree of polymerization of PCA, the amount of regulator introduced and the equilibrium concentration of water in the polymer melt.

The present paper is devoted to a theoretical discussion of the relationship between the quantities mentioned above, when the following compounds are used as regulators: monocarboxylic acids and monoamines, dicarboxylic acids and diamines, amine and amide salts.

Derivation of equations. Monocarboxylic acids and monoamines. When monocarboxylic acids are used as regulators, PCA macromolecules of two types should be formed:



and the equilibrium reactions in the polymer melt may be represented by the schemes:



If the concentration of macromolecules (the number of chains) in a weighed polymer sample is expressed in moles per basic mole, then \bar{P} for such a polymer is equal to $1/n$, where n is the number of chains. In the present case, $n = [-\text{COOH}]$.

In equilibrium, the concentration of the end carboxylic groups is given by

$$[-\text{COOH}]_{\text{eq}} = \frac{[-\text{NHCO}-]_{\text{eq}}(k'[\text{H}_2\text{O}]_{\text{eq}} + k_2[\text{RCOOH}]_0)}{k_1[-\text{NH}_2]_{\text{eq}} + k_2[-\text{NHCOR}]_{\text{eq}}} \quad (6)$$

Here k and k_2 are the rate constants for the reaction between end amino and acylamino groups with end carboxylic groups respectively; k' and k_1 are the rate constants for hydrolysis and acidolysis of macromolecular amide bonds.

Assuming that $[-\text{NHCO}-]_{\text{eq}} = 1$; $[-\text{NHCOR}]_{\text{eq}} = [\text{RCOOH}]_0 - [\text{RCOOH}]_{\text{eq}} = \Delta[\text{RCOOH}]_{\text{eq}}$; $[-\text{NH}_2]_{\text{eq}} = [-\text{COOH}]_{\text{eq}} - \Delta[\text{RCOOH}]_{\text{eq}}$ and substituting these values into equation (6), we obtain after some rearrangement

$$[-\text{COOH}]_{\text{eq}} = \frac{([\text{H}_2\text{O}]_{\text{eq}} + \alpha \cdot \frac{k_2}{k'} [\text{RCOOH}]_0)}{K \left([-\text{COOH}]_{\text{eq}} \left(1 - \frac{k_2}{k} \right) \Delta[\text{RCOOH}]_{\text{eq}} \right)}$$

880

L. N. Mikhovets and Yu. S. Patkachev

where

$$\alpha = \frac{[\text{RCOOH}]_{\infty}}{[\text{RCOOH}]_0}$$

In this case, the average degree of polymerization may be written in the form:

$$\bar{P} = \frac{K \left(\frac{1}{\bar{P}} - \left(1 - \frac{k_2}{K} \right) \Delta [\text{RCOOH}]_{\infty} \right)}{[\text{H}_2\text{O}]_{\infty} + \alpha \frac{k_2}{K} [\text{RCOOH}]_0} \quad (7)$$

By reducing (7) to a quadratic equation, solving it with respect to \bar{P} , and selecting the appropriate root, we obtain

$$\bar{P} = \sqrt{\frac{K^2 \left(1 - \frac{k_2}{K} \right)^2 \Delta [\text{RCOOH}]_{\infty}^2}{4 \left([\text{H}_2\text{O}]_{\infty} + \alpha \frac{k_2}{K} [\text{RCOOH}]_0 \right)^2}} + \frac{K}{[\text{H}_2\text{O}]_{\infty} + \alpha \frac{k_2}{K} [\text{RCOOH}]_0} - \frac{K \left(1 - \frac{k_2}{K} \right) \Delta [\text{RCOOH}]_{\infty}}{2 \left([\text{H}_2\text{O}]_{\infty} + \alpha \frac{k_2}{K} [\text{RCOOH}]_0 \right)}$$

According to the data of Korshak and Golubev [11], if the excess of one of the components does not exceed 2 mole %, the equilibrium acidolysis reaction (5) may be neglected. In this case, the equation for \bar{P} simplifies to:

$$\bar{P} = \sqrt{\frac{K^2 \Delta [\text{RCOOH}]_{\infty}^2}{4 [\text{H}_2\text{O}]_{\infty}^2}} + \frac{K}{[\text{H}_2\text{O}]_{\infty}} - \frac{K \Delta [\text{RCOOH}]_{\infty}}{2 [\text{H}_2\text{O}]_{\infty}} \quad (8)$$

and the dependence of α on \bar{P} may be written as the equation

$$\alpha = \frac{1}{1 + \frac{K_1}{K} \bar{P}} \approx \frac{K}{K_1 \bar{P}} \quad (9)$$

which may be easily derived from the equation for the concentration of end amino groups, found from equations (3) and (4).

By combining equations (8) and (9), we obtain the following equation after rearrangement:

$$\bar{P} = \sqrt{\frac{K^2 [\text{RCOOH}]_{\infty}^2}{4 [\text{H}_2\text{O}]_{\infty}^2}} + \frac{K (K [\text{RCOOH}]_0 + K_1)}{K_1 [\text{H}_2\text{O}]_{\infty}} - \frac{K [\text{RCOOH}]_0}{2 [\text{H}_2\text{O}]_{\infty}} \quad (10)$$

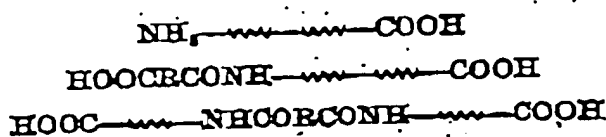
in which \bar{P} is a function only of the equilibrium water concentration in the melt and the initial concentration of monocarboxylic acid.

By applying all the considerations put forward above to POA containing a monoamine as regulator, we obtain equations similar to (10) and (9) for \bar{P} and α

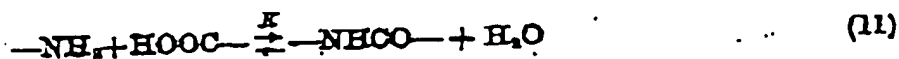
Regulation of molecular weight of polycaproamide

861

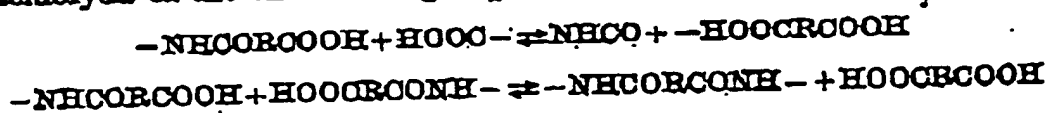
Dicarboxylic acids and diamines. Three types of macromolecule should be formed in the PCA melt in the presence of dicarboxylic acids:



and the equilibrium reactions may be represented by the schemes:



if the acidolysis of the end amide groups is neglected



From work on the amide equilibrium in polyhexamethylene adipamide [12, 13], it is expected that the values of K_1 and K_2 should be practically the same for dicarboxylic acids and aliphatic diamines, whereas they may be substantially different in the case of aromatic diamines in which the basicity of one of the amino groups is less than the basicity of the end amino group of PCA. In particular, the introduction of end aromatic groups into PCA by Bogdanov *et al.* was based on this [4].

It follows from equation (13) that

$$\frac{[\text{---NHCORCONH} \text{---}]_{\text{eq}}}{[\text{---NHCORCOOH}]_{\text{eq}}} = \frac{K_1 [\text{---NH}_2]_{\text{eq}}}{[\text{H}_2\text{O}]_{\text{eq}}}$$

If $[\text{---NH}_2]_{\text{eq}}/[\text{H}_2\text{O}]_{\text{eq}} > 0.1$, which is entirely feasible for values of \bar{P} of practical interest (Table 1), then $[\text{---NHCORCONH} \text{---}]_{\text{eq}} \ll [\text{---NHCORCOOH}]_{\text{eq}}$ since K_1 is of the order of several hundred [6, 8, 11]. In other words, dicarboxylic acids in PCA should exist almost entirely in the form of $\text{---NHCORCONH} \text{---}$, and consequently the concentration of the free acid which is determined by the concentration of $\text{---NHCORCOOH} \text{---}$ groups should be less than in the case of monocarboxylic acids.

From equation (12) and (13) it follows that

$$\begin{aligned} [\text{---NHCORCOOH}]_{\text{eq}} &= \frac{[\text{---NH}_2]_{\text{eq}} [\text{R}(\text{COOH})_2]_{\text{eq}} K_2}{[\text{H}_2\text{O}]_{\text{eq}}} \\ &= \frac{[\text{---NHCORCONH} \text{---}]_{\text{eq}} [\text{H}_2\text{O}]_{\text{eq}}}{K_1 [\text{---NH}_2]_{\text{eq}}}; \end{aligned}$$

$$\alpha \approx \frac{[\text{R}(\text{COOH})_2]_{\text{eq}}}{[\text{---NHCORCONH} \text{---}]_{\text{eq}}} = \left(\frac{[\text{H}_2\text{O}]_{\text{eq}}}{K_1 [\text{---NH}_2]_{\text{eq}}} \right)^2 \quad (14)$$

889

L. N. MIZEROVSKI and Yu. S. PALKACHEV

Since

$$\alpha = \frac{[R(COOH)]_{\alpha}}{[\sim\sim\sim NHCORCONH\sim\sim\sim]_{\alpha} + [\sim\sim\sim NHCORCOOH]_{\alpha} + [R(COOH)]_{\alpha}}$$

equation (14) should give somewhat overestimated values for the uncombined fraction of the acid.

In the presence of the dicarboxylic acid, the number of chains is determined by the relationship:

$$n = \frac{[\sim\sim\sim COOH]_{\alpha} + [\sim\sim\sim NH_2]_{\alpha}}{2} = [\sim\sim\sim COOH]_{\alpha} - (1-\alpha)[R(COOH)]_{\alpha},$$

and

$$\bar{P} = \frac{1}{[\sim\sim\sim COOH]_{\alpha} - (1-\alpha)[R(COOH)]_{\alpha}} \quad (15)$$

If $\alpha \ll 1$, the concentration of carboxyl groups at equilibrium is determined by equation (11) alone.

In this case, taking into account the fact that

$$[\sim\sim\sim NH_2]_{\alpha} = [\sim\sim\sim COOH]_{\alpha} - 2(1-\alpha)[R(COOH)]_{\alpha},$$

we find

$$[\sim\sim\sim COOH]_{\alpha} = (1-\alpha)[R(COOH)]_{\alpha} + \sqrt{(1-\alpha)^2[R(COOH)]_{\alpha}^2 + \frac{[H_2O]_{\alpha}}{K}}$$

Substitution of this equation into equation (15) gives

$$\bar{P} = \frac{1}{\sqrt{(1-\alpha)^2[R(COOH)]_{\alpha}^2 + \frac{[H_2O]_{\alpha}}{K}}} \quad (16)$$

On the basis of equations (14) and (15), the way in which α depends on \bar{P} may be obtained:

$$\alpha = \frac{[H_2O]_{\alpha}}{K_1^2 (1/\bar{P} - (1-\alpha)[R(COOH)]_{\alpha})^2} \quad (17)$$

If $\alpha \ll 1$,

$$\alpha = \frac{[H_2O]_{\alpha}}{K_1^2 (1/\bar{P} - [R(COOH)]_{\alpha})^2} \quad (18)$$

The simultaneous solution of equations (16) and (18) leads to a very cumbersome expression and it is therefore more convenient in calculations to treat equations (16) and (18) by the method of successive approximations, especially, as may be seen from the data in Table 1, because the value of α in equation (16) may generally be neglected.

In the case of diamines whose basicity is greater than or equal to the basicity of the end amino group, the expressions for \bar{P} and α are similar to those presented above. If the basicity of one of the amino groups of the diamine is substantially less than the basicity of the amino group of PCA, the diamine should then react

Regulation of molecular weight of polycaprosamide

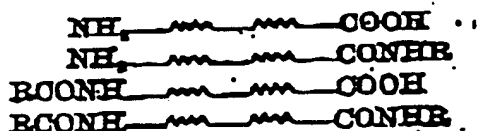
863

in effect as a monofunctional compound, that is, the equations (10) and (9) should hold for \bar{P} and α .

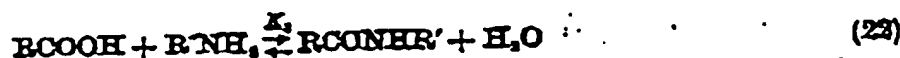
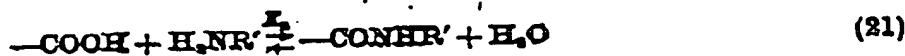
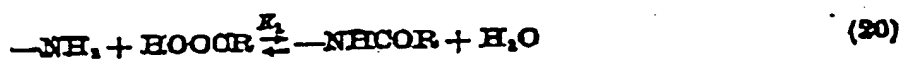
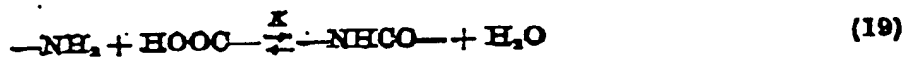
Amides and amine salts of carboxylic acids. The effects of amides and amine salts of carboxylic acids as molecular weight regulators for PCA must be essentially the same in principle, since, under conditions of hydrolytic polymerization of caprolactam, amine salts transform into the corresponding amides considerably before any marked quantity of PCA is formed.

A feature of amide regulators is that the reduction in the molecular weight of PCA in their presence is connected with the occurrence of amidolysis and it should consequently not upset the equimolecular ratio between the different kinds of end groups.

Four types of macromolecule are formed in the presence of these regulators:



The equilibrium reactions in the melt may be represented by the following schemes in this case:



Acidolysis and amidolysis of the free amide by end groups of the macromolecules, and the reaction $-\text{NHCO}- + \text{R}'\text{NHCO}- \rightleftharpoons -\text{NHCO}- + \text{RCONHR}'$ may be neglected.

If it is assumed that $K_1 \approx K_2$, then the concentrations of the free acid and the free amine will be equal and both will consequently be equal to the concentrations of end amino and carboxylic groups.

In this case, the number of chains will be given by:

$$\begin{aligned} n &= \frac{[-\text{COOH}]_{\text{eq}} + [-\text{NH}_2]_{\text{eq}} + [\text{RCONH}-]_{\text{eq}} + [\text{R}'\text{NHCO}-]_{\text{eq}}}{2} \\ &= [-\text{COOH}]_{\text{eq}} + 4[\text{RCONHR}']_{\text{eq}} = [-\text{NH}_2]_{\text{eq}} + 4[\text{RCONHR}']_{\text{eq}}. \end{aligned} \quad (23)$$

Here

$$\begin{aligned} 4[\text{RCONHR}']_{\text{eq}} &= [\text{RCONH}-]_{\text{eq}} = [\text{R}'\text{HNCO}-]_{\text{eq}} = [\text{RCONHR}']_{\text{eq}} \\ &= ([\text{RCOOH}]_{\text{eq}} + [\text{RCONHR}']_{\text{eq}}) = [\text{RCONHR}']_{\text{eq}} = ([\text{R}'\text{NH}_2]_{\text{eq}} + [\text{RCONHR}']_{\text{eq}}). \end{aligned}$$

By taking equation (23) into account, the expression for \bar{P} becomes:

$$\bar{P} = \frac{1}{[-\text{COOH}]_{\text{eq}} + 4[\text{RCONHR}']_{\text{eq}}} \quad (24)$$

884

L. N. MIZEROVSKI and Yu. S. PAIKACHEV

If it is assumed that at equilibrium $[-NH_2]_{eq} \gg [RNH_2]_{eq}$, the concentration of end carboxyl groups may be expressed from equation (19):

$$[-COOH]_{eq} = \sqrt{\frac{[H_2O]_{eq}}{K}}$$

Substitution of this expression into equation (24) gives

$$\bar{P} = \frac{1}{\sqrt{\frac{[H_2O]_{eq}}{K} + \Delta [RCONHR]_{eq}}} \quad (25)$$

Since the absolute magnitudes of $[RCOOH]_{eq}$ and $[RNH_2]_{eq}$ are small, reaction (22) may be neglected. In this case:

$$\begin{aligned} \Delta [RCONHR]_{eq} &= [RCONHR]_0 - [RCOOH]_{eq} \\ -[RCONHR]_0 + [RNH_2]_{eq} &= (1-\alpha) [RCONHR]_0 \end{aligned}$$

It follows from equations (19) and (20) that:

$$[RCOOH]_{eq} = \frac{[RCONHR]_0 \sqrt{K[H_2O]_{eq}}}{K_1 + \sqrt{K[H_2O]_{eq}}}$$

and

$$\alpha = \frac{[RCOOH]_{eq}}{[RCONHR]_0} = \frac{\sqrt{K[H_2O]_{eq}}}{K_1 + \sqrt{K[H_2O]_{eq}}} \quad (26)$$

Substitution of equation (26) into equation (25) gives the final expression for the degree of polymerization of PCA in the presence of water and amides:

$$\bar{P} = \frac{1}{\sqrt{\frac{[H_2O]_{eq}}{K} + \left(1 - \frac{\sqrt{K[H_2O]_{eq}}}{K_1 + \sqrt{K[H_2O]_{eq}}}\right) [RCONHR]_0}} \quad (27)$$

As far as we know, there is no systematic information in the literature about the way in which the constant for the amide equilibrium depends on the strength of the acid and amine, although the results of a number of authors [6, 8, 12, 13] point to a considerable interdependence of these quantities. It may be suggested on the basis of these results that the ratio K/K_1 for the various regulators in the temperature region 220–290°C must lie in the range 0.5–2.0, but with the evident exception of those cases when amines with a basicity much less than the basicity of the end amino group of PCA, and strong acids of the chloroacetic type are used.

If the ratio K/K_1 remains constant on going from a monocarboxylic acid (monoamine) to a dicarboxylic acid (diamine) or amide (amine salt), equations (10), (18) and (27) make it possible to assess quantitatively the differences in the regulating effects of these compounds.

Regulation of molecular weight of polycaproamide

865

Tables 1-3 show the results of calculations of \bar{P} and α for the cases when mono- and dicarboxylic acids and amides are used as regulators. It is here taken that $K=K_1=400$, corresponding to a temperature of 245°C and an equilibrium water content of 5×10^{-3} – 3×10^{-3} mole/basic mole [9].

TABLE 1. EFFECT OF CONCENTRATION OF DICARBOXYLIC ACIDS AND WATER ON THE PROPERTIES OF THE EQUILIBRIUM POLYCAPROAMIDE

Concentration, mole/basic mole		\bar{P}			$\alpha \times 10^3, \%$	β^*	$\frac{[-NH]_{eq}}{[H_2O]_{eq}}$
water	regulator	from eqn. (2)	from eqn. (1)	from eqn. (16)			
5×10^{-3}	—	288	—	—	—	1.000	0.706
	5×10^{-4}	—	2000	280	0.16	0.752	0.615
	1×10^{-3}	—	1000	272	0.22	0.570	0.536
	5×10^{-3}	—	200	164	1.30	0.101	0.224
	1×10^{-2}	—	100	94.5	4.33	0.029	0.120
	2×10^{-2}	—	50	49.3	17.3	0.008	0.060
	—	200	—	—	—	1.000	0.500
1×10^{-2}	5×10^{-4}	—	2000	199	0.31	0.820	0.452
	1×10^{-3}	—	1000	196	0.37	0.570	0.410
	5×10^{-3}	—	200	142	1.56	0.172	0.207
	1×10^{-2}	—	100	89.5	4.32	0.056	0.118
	2×10^{-2}	—	50	48.5	17.3	0.015	0.060
	—	200	—	—	—	1.000	0.500
	5×10^{-4}	—	2000	199	0.31	0.820	0.452

$$* \beta = \frac{[-NH]_{eq}}{[-COOH]_{eq}}$$

A comparison of the values of \bar{P} calculated from equation (2) and from equations (10) and (16) and (27) shows that the efficiencies of various types of regulator in the presence of water are different. They may be placed in the following order of increasing effectiveness: dicarboxylic acids (diamines), monocarboxylic acids (monoamines), amides (amine salts). In the last two cases, the presence of even 0.05 mole % of regulator reduces the value of \bar{P} of equilibrium PCA by 5–10%, which lies outside the limits of error in determining \bar{P} from end groups. Thus the dependence of \bar{P} on the concentration of monocarboxylic acids, shown in Table 2, is in good qualitative agreement with the experimental data of Mattes [5] on the polymerization of caprolactam in the presence of benzoic acid (taking into account the remark of Wiloth [12] that the concentration of water in these experiments was more than 1 mole %). Dicarboxylic acids and diamines should exert their presence the most fully, and monocarboxylic acids and monoamines the least.

It follows from a comparison of the values of \bar{P} calculated from equation (1) and from equations (10), (16) and (27) that even very small concentrations of water have a very strong effect on the polymerization of PCA synthesized in the presence of regulators, particularly when the regulator concentration is small.

The conditions that the values of \bar{P} calculated from these formulae should be equal are easily obtained if equation (1) is set equal to equations (10), (16) and (27) respectively.

After some elementary rearrangement we obtain: for monocarboxylic acids (monoamines) $[RCOOH]_0 = \sqrt[3]{\frac{K_1[H_2O]_0^3}{K}}$; for dicarboxylic acids (diamines) $\frac{[H_2O]_0}{K} = 0$; for amides (amine salts) $[RCONHR]_0 = \frac{K_1 + \sqrt{K[H_2O]_0}}{K}$.

It may easily be seen from the formulae presented that, if in the case of monocarboxylic acids (monoamines) and amides (amine salts) it is possible to obtain those ratios between the water and regulator concentrations for which equation (1) is true, then in the case of dicarboxylic acids (diamines) equation (1) is true only for $[H_2O]_0 = 0$.

TABLE 2. EFFECT OF CONCENTRATION OF MONOCARBOXYLIC ACIDS AND WATER ON THE PROPERTIES OF EQUILIBRIUM POLYCAPROAMIDE

Concentration, mole/basic mole		P			$\alpha, \%$	β
water	regulator	from eqn. (2)	from eqn. (1)	from eqn. (10)		
5×10^{-4} (0.08 wt. %)	—	283	—	—	—	1.000
	5×10^{-4}	—	2000	284	0.38	0.887
	1×10^{-3}	—	1000	248	0.41	0.764
	5×10^{-3}	—	2000	147	0.68	0.270
	1×10^{-2}	—	100	91	1.10	0.100
	2×10^{-2}	—	50	50	2.00	0.020
1×10^{-3} (0.10 wt. %)	—	200	—	—	—	1.000
	5×10^{-4}	—	2000	191	0.58	0.905
	1×10^{-3}	—	1000	180	0.56	0.820
	5×10^{-3}	—	300	124	0.81	0.380
	1×10^{-2}	—	100	84	1.19	0.170
	2×10^{-2}	—	50	48	2.10	0.058

Equations (10), (16) and (27) indicate that the equilibrium degree of polymerization of PCA synthesized in the presence of water and a molecular weight regulator depends both on the amount of regulator introduced and on the water concentration at equilibrium, as well as on the PCA macromolecules and on the end amide group formed through the reactions of the PCA macromolecules with the regulator.

In the general case these constants may be unequal, since the strength of the carboxylic acids and amines generally used as regulators differ considerably from the strength of the end groups of PCA and consequently the regulating effect of carboxylic acids and amines, and equally that of their salts, should to a certain extent depend on the constants and on their dissociation.

The introduction of regulators into PCA (apart from directly regulating molecular weight) also has the objective of increasing its resistance (stability) to additional polycondensation during repeated melting in the forming of components (in particular fibres [1-3, 14]). The increase in the stability of PCA is explained

Regulation of molecular weight of polyasproamide

857

by the fact that the regulators block off one or both end groups of the PCA macromolecule and consequently the end group concentration in the polymer and the rate of additional polycondensation are decreased.

TABLE 3. EFFECT OF CONCENTRATION OF AMIDES AND WATER ON THE PROPERTIES OF EQUILIBRIUM POLYCAPROAMIDES

Concentration, mole/basic mole		\bar{P}			$\alpha, \%$	β	$\frac{[\text{NH}]_{\text{eq}}}{[-\text{NH}]_{\text{eq}}^*}$
water	regulator	from eqn. (2)	from eqn. (1)	from eqn. (27)			
5×10^{-3}	—	288	—	—	—	1.0	1.000
	5×10^{-4}	—	2000	248	0.35	1.0	0.875
	1×10^{-3}	—	1000	221	0.85	1.0	0.780
	5×10^{-3}	—	800	117	0.35	1.0	0.412
	1×10^{-2}	—	100	74	0.35	1.0	0.262
	2×10^{-2}	—	50	42.6	0.35	1.0	0.150
1×10^{-2}	—	200	—	—	—	1.0	1.000
	5×10^{-4}	—	2000	182	0.50	1.0	0.910
	1×10^{-3}	—	1000	187	0.50	1.0	0.832
	5×10^{-3}	—	200	100	0.50	1.0	0.500
	1×10^{-2}	—	100	67	0.50	1.0	0.335
	2×10^{-2}	—	50	40	0.50	1.0	0.200

* $[-\text{NH}]_{\text{eq}}$ in the amine group concentration in PCA of the same molecular weight synthesized in the absence of a regulator.

This is in good qualitative agreement with data (see Table 1-3) according to which as the concentration of mono- and dicarboxylic acids is increased the ratio $[-\text{NH}]_{\text{eq}}/[-\text{COOH}]_{\text{eq}} = \beta$ continuously decreases, and as the amide

TABLE 4. DEPENDENCE OF THE RESISTANCE OF PCA TO ADDITIONAL POLYCONDENSATION ON THE TYPE AND CONCENTRATION OF THE MOLECULAR WEIGHT REGULATOR

Regulator	Concentration of regulator, mole/basic mole					
	0	5×10^{-4}	1×10^{-3}	5×10^{-3}	1×10^{-2}	2×10^{-2}
Monocarboxylic acid (monoamine)	1.41	1.38	1.37	1.19	1.08	1.04
Dicarboxylic acid (diamine)	1.41	1.406	1.39	1.16	1.06	1.02
Amide (amine salt)	1.41	1.36	1.32	1.17	1.10	1.06

(amine salt) concentration is increased, although this ratio remains constant, there is nevertheless a decrease in the overall number of end groups as compared with a polymer of the same molecular weight synthesized without a stabilizer.

It also follows from the data presented that β is reduced more rapidly by the introduction of dicarboxylic acids than by the introduction of monocarboxylic

acids. The explanation of this relationship is quite clear, since in the case of dicarboxylic acids the blocked amino groups are replaced by an equivalent number of carboxylic groups and this does not happen when monocarboxylic acids are introduced. It is also clear that when mono- and diamines are used as regulators the pattern should be similar with the exception that β will be greater than unity.

On the basis of the relationships (10), (16) and (27) obtained in the present work, it is possible to make a quantitative comparison of the stability of equilibrium PCA specimens synthesized in the presence or absence of regulators. We thus start on the basis of the fact that the direction of the polycondensation-hydrolysis process during the repeated melting of PCA depends on the way in which the relationship

$$K = \frac{[-\text{NHCO}-]_{\text{eq}} [\text{H}_2\text{O}]_{\text{eq}}}{[-\text{COOH}]_{\text{eq}} [-\text{NH}_2]_{\text{eq}}} \quad (28)$$

which had been established during the polymerization of caprolactam is disrupted during the technological treatment of PCA before the forming of components. During the manufacture of fibres, the disruption of this relationship occurs through the elimination of some proportion of the linear PCA oligomers during the extraction of low molecular weight cyclic compounds and caprolactam by water, i.e. the disruption occurs through a reduction in the denominator and a change in the moisture content of the polymer as compared with the moisture content of the melt at the end of the polymerization reaction; and through a change in the numerator.

Since additional polycondensation takes place as a rule, it may be concluded that the numerator in equation (28) is reduced to a greater extent than the denominator. In this case, if it is assumed that the changes in the end group concentration during the extraction of stabilized and unstabilized PCA are the same, the ratio of the values of \bar{P} for specimens synthesized with various equilibrium water concentrations may be chosen as a criterion of the stability of PCA under repeated melting (the smaller the difference between \bar{P} , the more stable the polymer).

In order to illustrate possible trends in the stability of PCA synthesized in the presence of various regulators, Table 4 presents values of the \bar{P} ratios calculated for two concentrations taken from Tables 1-3, as a function of the concentration and type of regulator.

It may be seen that the stability of PCA is markedly raised as the concentration of the molecular-weight regulator is increased, but on the basis of these data, it is clearly impossible to look for any marked differences in the stability of equilibrium PCA obtained in the presence of regulators with different structures. Therefore the data in the literature [14] about the marked differences in the stability of PCA synthesized in the presence of acetic acid, *n*-butylamine, *n*-butylamine acetate and adipic acid, must be considered as relating to polymers in which the amide equilibrium was not reached during the polymerization of caprolactam.

Regulation of molecular weight of polycaproamide

869

CONCLUSIONS

(1) A theoretical discussion has been given of the effect of regulators with various structures on the molecular weight of polycaproamide.

(2) Equations have been presented which connect the degree of polymerization of polycaproamide with the equilibrium concentration of water and the concentrations of mono- and bifunctional regulators.

(3) It has been shown that amide regulators have the greatest effect on the degree of polymerization of PCA in the presence of water, and dicarboxylic acids and diamines have the least effect.

(4) It has been shown that the stability of equilibrium polycaproamide under repeated melting depends little on the type of molecular weight regulator used.

Translated by G. F. MODDER

REFERENCES

1. Z. A. ROGOVIN, *Osnovy khimii i tekhnologii khimicheskikh volokon* (Principles of the Chemistry and Technology of Chemical Fibres). Vol. II, p. 38, Izd. "Khimiya", 1964
2. E. Ya. FISHMAN and N. A. KHRUZIN, *Proizvodstvo volokna capron* (Production of Capron Fibres). p. 27, Izd. "Khimiya", 1967
3. H. KLARE, E. FRITSCH and A. GROEBE, *Sinteticheskie poliamidnye volokna* (Synthetic Polyamide Fibres). p. 101, 246, Izd. "Mir", 1966 (Russian translation)
4. M. N. BOGDANOV, A. U. LESHCHINER and L. A. PLYASHKEVICH, *Vysokomol. soyed.* 8: 903, 1968 (Translated in *Polymer Sci. U.S.S.R.* 8: 5, 993, 1966)
5. A. MATTES, *Makromolok. Chem.* 5: 203, 1951
6. F. WILOTH, *Z. phys. Chem.* 5: 66, 1955
7. P. H. HERMANS, *J. Appl. Polymer Sci.* 5: 493, 1955
8. O. FUKUMOTO, *J. Polymer Sci.* 22: 283, 1956
9. A. B. MAGGY, *J. Chem. Soc.*, 798, 1953
10. H. KLARE, E. FRITSCH and A. GROEBE, *Sinteticheskie poliamidnye volokna* (Synthetic Polyamide Fibres). p. 173, Izd. "Mir", 1966 (Russian translation)
11. V. V. KORSHAK and V. V. GOLUBEV, *Izv. AN SSSR, Otd. khim. nauk*, 186, 1946
12. F. WILOTH, *Makromolok. Chem.* 15: 98, 108, 1955
13. H. OGATA, *Makromolok. Chem.* 42: 52, 1960
14. I. ALEKSANDRU, M. KOMAN, T. RIZESCU and A. POPOVICH, *Khimich. volokna*, No. 4, 4, 1962

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



PCT
WELTORGANISATION FÜR GEISTIGES EIGENTUM
Internationales Büro
INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE
INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

<p>(51) Internationale Patentklassifikation ⁷ : G02B 1/04, 6/16</p>	A1	<p>(11) Internationale Veröffentlichungsnummer: WO 00/60382</p> <p>(43) Internationales Veröffentlichungsdatum: 12. Oktober 2000 (12.10.00)</p>
<p>(21) Internationales Aktenzeichen: PCT/EP00/02831</p> <p>(22) Internationales Anmeldedatum: 30. März 2000 (30.03.00)</p> <p>(30) Prioritätsdaten: 199 14 743.4 31. März 1999 (31.03.99) DE</p> <p>(71) Anmelder (für alle Bestimmungsstaaten ausser US): SIEMENS AKTIENGESELLSCHAFT (DE/DE); Wittelsbacherplatz 2, D-80333 München (DE). EMS-CHEMIE AG (CH/CH); Reichenauerstrasse, CH-7013 Domat/Ems (CH).</p> <p>(72) Erfinder; und</p> <p>(75) Erfinder/Anmelder (nur für US): HORN, Hans-Matthias (DE/DE); Regerweg 5, D-96465 Neustadt (DE). SCHAEFER, Joachim (DE/DE); Obere Birkleite 15, D-96465 Neustadt (DE). SCHMIDT, Ilona (DE/DE); Am Tau 2, D-96465 Neustadt (DE). THULLEN, Helmut (DE/CH); Versamerstrasse 39, CH-7402 Bonaduz (CH). EICH-HORN, Volker (DE/CH); Ringstrasse 170, CH-7000 Chur (CH). WUTKE, Thomas (DE/DE); Denklinger Strasse 79, D-51545 Waldbröl (DE). STOEPELMANN, Georg (DE/CH); Via Sableun 2, CH-7402 Bonaduz (CH).</p> <p>(74) Anwalt: BECKER-KURIG-STRAUS; Bavariastrasse 7, D-80336 München (DE).</p>		<p>(81) Bestimmungsstaaten: AU, BR, CA, CN, CZ, IN, JP, KR, MX, SG, SK, TR, US, europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Veröffentlicht <i>Mit internationalem Recherchenbericht.</i></p>
<p>(54) Title: OPTICAL WAVE-GUIDE</p> <p>(54) Bezeichnung: OPTISCHE ADER</p> <p>(57) Abstract</p> <p>The car industry makes increasing use of plastic light guides whose protective layers (4) consist of a polyamide. Since unmodified polyamide adheres poorly to the fluoropolymers frequently used as material for the fibre cladding (3), the plastic light guide (2, 3) moves in relation to the protective layer (4) when the temperature changes. To suppress this so-called 'pistoning' effect the light guide plugs and support elements have to exert considerable clamping forces on the protective layer (4) and the plastic light guide (2, 3) positioned therein, which results in greater signal attenuation. The use of a modified polyamide significantly improves the adhesion of the protective layer (4) on the fluoropolymer cladding (3) of a plastic light guide. A modified polyamide 12 whose carboxyl terminal group concentration is no more than 15 µAq/g and whose amino terminal group concentration is between 50 µAq/g and 300 µAq/g and which presents low viscosity is especially suitable as protective layer material.</p> <p>(57) Zusammenfassung</p> <p>Im Bereich der Automobilindustrie kommen zunehmend K-LWL zum Einsatz, deren Schutzhülle (4) aus einem PA besteht. Da unmodifiziertes PA nur schlecht auf dem häufig als Material für den Fasermantel (3) verwendeten Fluorpolymeren haftet, bewegt sich der K-LWL (2, 3) bei einer Temperaturänderung relativ zur Schutzhülle (4). Um diesen als "Pistoning" bezeichneten Effekt zu unterdrücken, müssen die LWL-Stecker und Halterungen sehr grosse, zu einer Erhöhung der Signaldämpfung führende Klemmkraft auf die Schutzhülle (4) und den darin angeordneten K-LWL (2, 3) ausüben. Durch Verwendung eines modifizierten PA lässt sich der Haftsitz der Schutzhülle (4) auf dem aus einem Fluorpolymer bestehenden Mantel (3) eines K-LWL deutlich verbessern. Als Schutzhüllenmaterial kommt insbesondere ein modifiziertes PA 12 in Betracht, dessen Carboxylendgruppenkonzentration maximal 15 µÄq/g beträgt und dessen Aminoendgruppenkonzentration im Bereich zwischen 50 µÄq/g und 300 µÄq/g liegt und tiefviskos ist.</p>		

INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

PCT/EP 00/02831

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G02B1/04 G02B6/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 239 935 A (ASAHI GLASS CO LTD) 7 October 1987 (1987-10-07) claims 1-8 page 7, line 27 - line 50 page 8, line 1 - line 11 ---	1
A	EP 0 883 001 A (TORAY INDUSTRIES) 9 December 1998 (1998-12-09) claims 1-15 page 7, line 26 - line 29 ---	1
A	WO 95 24450 A (HENKEL KGAA ;HEUCHER REIMAR (DE); MAASSEN ULRIKE (DE); KOPANNIA SI) 14 September 1995 (1995-09-14) claims 1-8 page 10, paragraph 1 --- -/--	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

3 July 2000

Date of mailing of the international search report

12/07/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo.nl,
Fax: (+31-70) 340-3018

Authorized officer

Depijper, R

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 00/02831

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 767 190 A (INVENTA AG) 9 April 1997 (1997-04-09) cited in the application claims 1-11 ---	1
A	GB 2 198 258 A (EMS-INVENTA AG.) 8 June 1988 (1988-06-08) claims 1-7 page 5, line 19 - line 32 page 7, line 22 - line 25 ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 016, no. 390 (P-1405), 19 August 1992 (1992-08-19) & JP 04 127107 A (ASAHI CHEM IND CO LTD), 28 April 1992 (1992-04-28) abstract -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/02831

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0239935	A	07-10-1987	JP 1953774 C	28-07-1995
			JP 6079095 B	05-10-1994
			JP 62232601 A	13-10-1987
			DE 3771758 A	05-09-1991
			US 4804246 A	14-02-1989
EP 0883001	A	09-12-1998	JP 10160947 A	19-06-1998
			WO 9823982 A	04-06-1998
WO 9524450	A	14-09-1995	DE 4408277 A	14-09-1995
			AT 166100 T	15-05-1998
			DE 59502172 D	18-06-1998
			EP 0749463 A	27-12-1996
			JP 9509978 T	07-10-1997
			US 5883172 A	16-03-1999
EP 0767190	A	09-04-1997	DE 19537003 A	10-04-1997
			JP 9194815 A	29-07-1997
			US 5804670 A	08-09-1998
			US 5869157 A	09-02-1999
			US 5869190 A	09-02-1999
GB 2198258	A	08-06-1988	CH 669678 A	31-03-1989
			CN 1033824 A	12-07-1989
			DE 3724997 A	04-08-1988
			FR 2606782 A	20-05-1988
			IT 1211918 B	08-11-1989
			JP 63139035 A	10-06-1988
			SE 465541 B	23-09-1991
			SE 8704413 A	18-05-1988
			US 4936651 A	26-06-1990
JP 04127107	A	28-04-1992	JP 2938951 B	25-08-1999

Grilamid (nylon 12) provides the lowest moisture absorption of any commercially available nylon, thus providing dimensional stability with mechanical properties virtually unaffected by environmental humidity.

Grilamid®
EMS

Grilamid L16

Grilamid L16 is a high flow extrusion grade, it has low viscosity and provides high resistance to environmental humidity.

Nomenclature

L Unreinforced nylon 12 grade

16 Low viscosity

Use Grilamid L16 for

For blown and cast film for direct contact with non alcoholic foodstuff.

Applications

- Rigid beverage tubes
- Food packaging
- Sausage skins
- Boiling bags
- freezer bags
- Plates
- Pipes
- Rods
- and many more ...

Availability

All grades are supplied pre-dried, packaged in moisture-proof, foil-lined bags containing 25kg (55.1lbs). Other packaging can be made available

Listings

- FDA Regulations CFR21 paragraph 177.1500 (Direct contact, natural only)

Disclaimer

No liability is assumed and no representations or warranties, either express or implied, are made with respect to the information or the product to which the information refers.

[Download the Technical Data Sheet of Grilamid L16](#)

[Download the Material Safety Data Sheet of Grilamid L16 Natural](#)

 **back**

Grilamid (nylon 12) provides the lowest moisture absorption of any commercially available nylon, thus providing dimensional stability with mechanical properties virtually unaffected by environmental humidity.

Grilamid®
EMS

Grilamid L16 A

Grilamid L16 A is a low viscosity extrusion grade, hydrolysis stabilized.

Nomenclature

L Unreinforced nylon 12 grade

16 Low viscosity

A Hydrolysis stabilized

Use Grilamid L16 A for

Tubing and cable sheathings requiring hydrolysis resistance.

Applications

- Tubing and cable sheathings
- Profiles and many more ...

Availability

All grades are supplied pre-dried, packaged in moisture-proof, foil-lined bags containing 25kg (55.1lbs). Other packaging can be made available

Disclaimer

No liability is assumed and no representations or warranties, either express or implied, are made with respect to the information or the product to which the information refers.

Download the Technical Data Sheet of Grilamid L16 A (will be available soon)
Download the Material Safety Data Sheet of Grilamid L16 A (Natural)

 **back**

TECHNISCHES MERKBLATT

GRILAMID L16 LM

Produktbeschreibung

Grilamid L16 LM ist ein tiefviskoser Extrusionstyp auf Basis von Polyamid 12 (PA12).

Grilamid L16 LM ist UV- und hitzestabilisiert.

Die Modifikation mit einem Kristallisationsbeschleuniger bewirkt eine geringe Nachkristallisation und eine geringe Nachschwindung.

Die Hauptvorteile von Grilamid L16 LM sind:

- UV- und hitzebeständig
- Hohe Abrasionsfestigkeit
- Sehr gute Chemikalienbeständigkeit
- Sehr gute Ölbeständigkeit
- Hohe Oberflächengüte
- Gute Dimensionsstabilität
- Hohe Prozessgeschwindigkeit
- Niedrige Dichte, geringes Gewicht

Anwendungsbeispiele

Grilamid L16 LM eignet sich besonders für dünnwandige, mit hoher Geschwindigkeit extrudierte Kabel-Aussenummantelungen, die Sekundärisolation von Lichtwellenleitern und Kupferdraht-Isolationen im Elektro-/Elektronikbereich.

Grilamid®
EMS

EIGENSCHAFTEN

Mechanische Eigenschaften

		Norm	Einheit	Status	Grilamid L 16 LM
Zug-E-Modul	1 mm/min	ISO 527	MPa	kond.	1100
Streckspannung	50 mm/min	ISO 527	MPa	kond.	45
Streckdehnung	50 mm/min	ISO 527	%	kond.	15
Bruchspannung	50 mm/min	ISO 527	MPa	kond.	50
Bruchdehnung	50 mm/min	ISO 527	%	kond.	> 50
Schlagzähigkeit	Charpy, 23°C	ISO 179/2-1eU	kJ/m²	kond.	ohne Bruch
Schlagzähigkeit	Charpy, -30°C	ISO 179/2-1eU	kJ/m²	kond.	ohne Bruch
Kerbschlagzähigkeit	Charpy, 23°C	ISO 179/2-1eA	kJ/m²	kond.	7
Kerbschlagzähigkeit	Charpy, -30°C	ISO 179/2-1eA	kJ/m²	kond.	6
Shorehärte D		ISO 868	-	kond.	70

Thermische Eigenschaften

Schmelztemperatur	DSC	ISO 11357	°C	trocken	178
Formbeständigkeit HDT/A	1.80 MPa	ISO 75	°C	trocken	50
Formbeständigkeit HDT/B	0.45 MPa	ISO 75	°C	trocken	125
Therm. Längenausdehnung längs	23-55°C	ISO 11359	10 ⁻⁴ /K	trocken	1.2
Therm. Längenausdehnung quer	23-55°C	ISO 11359	10 ⁻⁴ /K	trocken	1.4
Maximale Gebrauchstemperatur	dauernd	ISO 2578	°C	trocken	90 - 110
Maximale Gebrauchstemperatur	kurzzeitig	ISO 2578	°C	trocken	150

Elektrische Eigenschaften

Durchschlagfestigkeit		IEC 60243-1	kV/mm	kond.	32
Vergleichende Kriechwegbildung	CTI	IEC 60112	-	kond.	600
Spez. Durchgangswiderstand		IEC 60093	Ω · m	kond.	10 ¹¹
Spez. Oberflächenwiderstand		IEC 60093	Ω	kond.	10 ¹²

Allgemeine Eigenschaften

Dichte		ISO 1183	g/cm³	trocken	1.01
Brennbarkeit (UL94)	0.8 mm	ISO 1210	Stufe	-	HB
Wasseraufnahme	23°C/gesätt.	ISO 62	%	-	1.5
Feuchtigkeitsaufnahme	23°C/50% r.F.	ISO 62	%	-	0.7
Linearer Spritzschwind	längs	ISO 294	%	trocken	0.80
Linearer Spritzschwind	quer	ISO 294	%	trocken	0.85

Produkt-Bezeichnung nach ISO 1874: PA12, EHLS, 14- 010N

Verarbeitungshinweise für die Extrusionsverarbeitung von Grilamid L 16 LM

Das vorliegende technische Merkblatt für Grilamid L 16 LM gibt Ihnen nützliche Hinweise für die Materialvorbereitung, die Maschinenanforderungen, den Werkzeugbau sowie die Verarbeitung.

MATERIALVORBEREITUNG

Grilamid L 16 LM wird verarbeitungsfertig getrocknet geliefert. Die Säcke sind luftdicht verschweisst. Eine Vortrocknung ist daher nicht erforderlich.

Lagerung

Verschweisste, unbeschädigte Säcke können, witterungsgeschützt, über Jahre gelagert werden. Als Lagerort empfiehlt sich ein trockener Raum, in dem die Säcke auch vor Beschädigung geschützt sind.

Handhabung und Sicherheit

Detaillierte Informationen können dem „Material Sicherheits Datenblatt“ (MSDS) entnommen werden, welches mit der Materialbestellung angefordert werden kann.

Trocknung

Grilamid L 16 LM wird bei der Herstellung auf einem Wassergehalt von $\leq 0.10\%$ getrocknet und luftdicht verpackt. Sollte die Verpackung beschädigt oder das Material zu lange offen gelagert worden sein, so muss das Granulat getrocknet werden. Ein zu hoher Wassergehalt reduziert die optischen und mechanischen Eigenschaften des Extrusionsartikels.

Die Trocknung kann erfolgen im:

Trockenlufttrockner

Temperatur:	max. 80°C
Zeit:	6 - 16 Stunden
Taupunkt der Trockenluft:	-25°C

Vakuumofen

Temperatur:	max. 100°C
Zeit:	4 - 12 Stunden

Trocknungstemperatur

Einen Hinweis auf eine oxidative Schädigung von Polyamiden gibt bei hellen Farben eine sichtbare Vergilbung. Im Trockenlufttrockner sollte die maximale Temperatur (80°C) nicht überschritten werden. Im Vakuumofen, bei geringerem Sauerstoffpartialdruck, ist eine höhere Temperatur (100°C) möglich. Um eine Vergilbung bei hellen Farben zu erkennen, ist es sinnvoll, eine kleine Granulatmenge als Vergleichsmuster zurückzuhalten.

Bei längeren Verweilzeiten im Maschinentrichter (über 1 Stunde) ist eine Trichterbeheizung oder ein Trichtertrockner (80°C) sinnvoll.

MASCHINENANFORDERUNGEN

Grilamid L 16 LM lässt sich auf allen für Polyamid geeigneten Maschinen verarbeiten.

Schnecke

Verschleissgeschützte Universalschnecken sind zu empfehlen (3 Zonen).

Schnecke

Länge:	24 D - 25 D
Kompressionsverhältnis:	2.8:1 - 3.5:1

Genutete Einzugsbuchsen

Für das Extrudieren von Grilamid L 16 LM empfehlen wir glatte Einzugsbuchsen. Zur Erzielung höherer spezifischer Ausstossleistungen kann die Einzugszone auf eine Länge von ca. 2 D nach der Einfüllöffnung leicht genutet werden (Nutentiefe max. 0.5 mm). Es wird empfohlen die Trichterzone auf konstante 60 - 90°C zu temperieren.

VERARBEITUNG

Grundeinstellungen

Als Grundeinstellung für die Verarbeitung von Grilamid L 16 LM hat sich folgendes Profil bewährt:

Temperaturen

Trichterzone	60 - 90°C
Einzugszone	160 - 170°C
Kompressionszone	190 - 200°C
Meteringzone	200 - 220°C
Flansch	200 - 220°C
Werkzeug	200 - 220°C
Düse	200 - 220°C
Masse	200 - 220°C
Kühlbadtemperatur	15 - 40°C

KUNDENDIENSTLEISTUNGEN

EMS-GRIVORY ist Spezialist in der Polyamidsynthese und Polyamidverarbeitung. Unsere Dienstleistungen umfassen nicht nur die Herstellung und Lieferung von technischen Thermoplasten, wir bieten vielmehr auch eine vollständige technische Unterstützung an:

- Rheologische Formteilauslegung / FEM
- Materialauswahl
- Verarbeitungsunterstützung
- Formteil- und Werkzeugdesign

Detaillierte Informationen zur Extrusion von EMS-Polyamiden finden Sie in unserem technischen Merkblatt „Rohrextrusion“.

Wir beraten Sie gerne. Nehmen Sie einfach Kontakt mit unseren Verkaufsbüros auf.

Die vorliegenden Daten und Empfehlungen entsprechen dem heutigen Stand unserer Erkenntnisse, eine Haftung in Bezug auf Anwendung und Verarbeitung kann jedoch nicht übernommen werden.

HAR/08.2001
www.emsgrivory.com